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Bi quantum dots implanted 2D C-doped BiOCl nanosheets: Enhanced visible light photocatalysis efficiency and reaction pathway

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ARTICLE INFO

Article history:

Received 13 February 2020

Accepted 10 March 2020

Published 5 September 2020

Keywords:

BiOCl

Carbon doping

Bi quantum dot

Photocatalysis

Reaction mechanism

ABSTRACT

The simultaneous integration of heteroatom doping and surface plasmon resonance (SPR) modulation on semiconductor photocatalysts could be capable of improving visible light utilization and charge separation, achieving better solar light conversion and photocatalysis efficiency. For this purpose, we have designed a novel Bi quantum dots (QDs) implanted C-doped BiOCl photocatalyst (C/BOC/B) for NO_x removal. The feasibility was firstly evaluated through density functional theory (DFT) calculations methods, which indicates that the enhanced photocatalytic performance could be expected owing to the synergistic effects of doped C heteroatoms and loaded Bi QDs. Then, the C/BOC/B was synthesized via a facile hydrothermal method and exhibited efficient and stable visible light photocatalytic NO removal. The results found that the doped C atoms can serve as electron guides to induce oriented charge transfer from Bi QDs to BiOCl, while the Bi QDs can act as light-capture and electron-donating sites. The reaction pathway and mechanism for NO conversion was unveiled by in situ Fourier-transform infrared spectroscopy combined with DFT calculation. The enhanced adsorption of reactants and intermediates could promote the overall reaction efficiency and selectivity in photocatalytic NO conversion. This work could provide a new perspective on the mechanistic understanding of the synergistic effects toward non-metal doping and SPR effects in semiconductor photocatalysts, and this presented technique could be extended for other semiconductor materials.

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1. Introduction

The heterogeneous photocatalysis has attracted increasing attention and represents a promising strategy for efficiently harvesting solar energy to solve the energy and environmental

issues [1–5]. Typical heterogeneous photocatalysis is realized via the following process: i) light-harvesting, ii) charge separation and delivery, and iii) photochemical redox reactions triggered by charge carriers [6,7]. Thus, developing active and durable photocatalysts with efficient solar utilization, low recom-

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This work was supported by the National Natural Science Foundation of China (21822601, 21777011), the Fundamental Research Funds for the Central Universities (ZYGX2019Z021, 2672018ZYGX2018J088), the Plan for “National Youth Talents” of the Organization Department of the Central Committee, the 111 Project (B20030), and Key R&D Program from Department of Science and Technology of Sichuan Province (2019YFG0319).

DOI: 10.1016/S1872-2067(20)63612-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 9, September 2020

bination rate and high transformation efficiency of carriers, are of extreme significance for improving the photocatalytic efficiency for its practical applications towards environmental remediation and solar energy conversion.

Two-dimensional (2D) materials have been widely applied in photocatalysis, electrocatalysis, and biomedical sciences, etc. [8–13]. Among them, the bismuth oxychloride (BiOCl, labeled as BOC) has been regarded as one of the most promising 2D photocatalysts attributed to its unique 2D morphology and adjustable electronic structure [14–16]. However, the efficiency of pristine BOC for photocatalysis is still unsatisfactory due to its intrinsic photo-chemically sluggish nature under visible light excitation [14,17,18]. The layered morphology of BOC can effectively reduce the migration distance of photo-generated charge from interior to surface. However, the immaculate 2D structure also leads to a regular surface charge configuration. Thus, the photo-excited carriers transfer randomly without extra restraint, triggering a high recombination rate of electron-hole pairs [19]. Therefore, further modification of BOC to adjust the sluggish electronic structure and steer the electrons' delivery direction for achieving better photocatalytic performance is highly desirable.

Elemental doping is one of the most efficient routes to improve the photocatalytic performance of BOC, mostly through narrowing the bandgap and restraining the recombination of photo-excited carriers [20–23]. Compared to diverse doping strategies, C doping is regarded as a promising approach to improve the photocatalytic activity of BOC by promoting photo-generated charge separation, directional transfer [24] and UV-response photocatalytic activity [25]. However, the actual performance of these C doped BOC (labeled as C/BOC) under visible light irradiation is still far from practical application owing to the intrinsic inferior quantum efficiency of BOC. Also, the multifunctional roles of carbon doping in photocatalysis have not been fully unraveled.

To further enhance the visible light response ability, integrating nanoscale plasmonic metal into semiconductor photocatalysts has been utilized as an intriguing method [26–28]. Significantly, in comparison with these conventional noble metal elements (Au, Ag, Cu, etc.), Bismuth (Bi), as a cheaper semimetal, exhibits a highly anisotropic Fermi surface, low carrier density, small carrier effective mass, and long carrier mean free path [29–31]. Moreover, more advantages in constructing Bi deposited BOC (labeled as BOC/B) composite photocatalyst have been revealed. For example, as one component of BOC, the in situ deposition of Bi quantum dots (QDs) onto BOC with better lattice matching in the interface is easy to implement. Besides, benefitted from the excellent visible light utilization induced by surface plasmon resonance (SPR) properties, which originated from the collective oscillation of its surface electrons, the hot electrons can transfer from the plasmonic Bi to BOC efficiently [32,33]. Thus, the visible light utilization and the charge carrier generation are increased effectively [29]. Unfortunately, the further transfer of these injected hot electrons to adsorbed reactant molecules is still severely restricted by the inefficient electron directional delivery and high recombination rate of charge carriers in the pristine BOC

layer [19]. Encouraged by the advanced modulate ability of C doping toward BOC electronic structure and unique properties of Bi metal, the simultaneous introduction of C doping and Bi loading into the BOC photocatalyst would be a promising strategy for improving the performance of BOC by strengthening the visible light utilization, electron donation, and directional electron delivery simultaneously. Thus, the developing of C doped BOC with plasmonic Bi modification (labeled as C/BOC/B) could be a feasible and valid route to enhance the photocatalytic performance and accelerate its practical applications. Meanwhile, revealing the synergistic effect between C doping and Bi deposition as well as the reaction mechanism during the photocatalytic process is also an important issue.

Inspired by the above considerations, we first evaluated the theoretical support and feasible guidance of this combined Bi loading and C doping strategy for improving the photocatalytic performance of BOC. Theoretical results confirmed that these doped C atoms can serve as electron guides to induce oriented charge transfer from Bi QD to BOC, while the plasmonic Bi QD can act as light-capture and electron-donating sites. Under the guidance of density functional theory (DFT) simulation results, the C/BOC/B sample was subsequently synthesized through a facile solvothermal method. It was revealed that the extraneous C atoms were successfully incorporated into the BOC lattice and in situ generated plasmonic Bi QDs were also distributed uniformly on the surface of BOC. It is proposed that this novel C/BOC/B photocatalyst exhibited outstanding photocatalytic efficiency toward NO purification compared with the pristine BOC or C/BOC. The reaction mechanism for NO conversion was then investigated via a combined experimental and theoretical method. The new approaches presented in this work can create more opportunities to enhance the photocatalytic performance of other potential 2D nanomaterials, thereby promoting the wide application of 2D nanomaterials in heterogeneous photocatalysis.

2. Experimental

2.1. DFT calculations

All DFT calculations were conducted in the “Vienna ab initio simulation package (code VASP5.4)” and a generalized gradient correlation functional. The cut-off energy and the Gaussian smearing width were respectively set to 400 and 0.2 eV. The Brillouin zone was sampled with a $3 \times 3 \times 1$ K points. All atoms were converged to 0.03 eV/Å. A hybrid Heyd-Scuseria-Ernzerhof (HSE06) method was utilized to predict the exact band structures.

The adsorption energy (E_{ads}) is defined as: $E_{\text{ads}} = E_{\text{tot}} - (E_{\text{s}} + E_{\text{mol}})$, where E_{tot} , E_{s} , and E_{mol} depict the total energy of the adsorption complex, the pure catalyst, and the isolated molecule, respectively.

2.2. Catalyst preparation

All reagents involved in this work were commercial products of analytical grade and were used directly without further

purification. The C/BOC sample was synthesized via a solvothermal method. Typically, 4 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 4 mmol KCl and 2.5 mmol glucose were dissolved into 60 mL distilled water. After being stirred vigorously for 30 min, the resulting mixture was sealed in a 100 mL polytetrafluoroethylene (PTFE) stainless steel autoclave and maintained at 180 °C for 18 h. After cooling down to room temperature, the resulting precipitate was washed with ethanol and deionized water three times and dried at 60 °C overnight to obtain the final C/BOC powder. The preparation of pure BOC is similar to that of C/BOC without the addition of glucose.

The C/BOC/B samples were prepared through the in situ post-deposition processes. Typically, 2 mmol of the as-prepared C/BOC powder was dispersed into 100 mL distilled water which contained 1.0 g PVP, and this mixture was vigorously stirred for 20 min. Then, a 40 mL NaBH_4 solution (37.5 mmol L^{-1} , the process of optimizing concentration was showed in Supporting Information) was dripped slowly into the solution. Mix the solution thoroughly for 1 h and let it stand for 1 h. The resulting precipitate was washed with ethanol and deionized water several times and dried at 50 °C to obtain C/BOC/B samples.

2.3. Characterization of catalysts

X-ray diffraction (XRD) with $\text{Cu } K_\alpha$ (Model D/Max RA, Rigaku Co., Japan) was carried out to confirm the crystal structure of these samples. Scanning electron microscopy (SEM, Model JSM-6490, Japan) and transmission electron microscopy (TEM, Model JEM-2010, Japan) were used for surface morphology characterization. X-ray photoelectron spectroscopy (XPS) was implemented with $\text{Al } K_\alpha$ X-rays (Thermo ESCALAB 250, Thermo Scientific, Waltham, MA, USA) as the excitation source to investigate the surface properties of catalysts. The light absorption property was measured by UV-vis diffuse reflectance spectra (DRS) (UV2550, Shimadzu, JPN) and photoluminescence (PL) spectra (F-7000, Hitachi, Japan). Electron spin resonance (ESR) spectra were utilized to measure the involvement of active radicals.

2.4. Visible light photocatalytic NO removal

The photocatalytic activities were investigated by monitoring the concentration of NO at ppb levels in a continuous-flow reactor, and this evaluation method was established according to our previous work [34]. Typically, 0.2 g catalyst was divided into two glass disks and was redispersed uniformly by ultrasonic treatment. After being dried at 50 °C, the two disks were installed into a reactor where a 150 W of commercial tungsten halogen lamp was placed vertically outside. An UV-cutoff filter was used to eliminate the light less than 420 nm. When the concentration of NO reached the adsorption-desorption equilibrium, the lamp was activated and a NO_x analyzer (Thermo Scientific, 42i-TL, USA) was used to analyze and record the NO_x concentration continuously. The NO removal ratio (η) was calculated by the following equation: $\eta = 1 - C/C_0$, where C and C_0 represent the equilibrium and initial NO concentration, respec-

tively.

2.5. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) investigation

In situ DRIFTS measurements were carried out on a Tensor II FT-IR spectrometer (Bruker, GER), which equipped with an in situ diffuse reflectance cell [24]. In a typical testing process, photocatalyst was put into the reaction cell. Then, the temperature was lifted to 300 °C to remove the residual hydrocarbons, H_2O , and CO_2 under the constant He gas flow (100 mL min^{-1}). The mixed reaction gases (50 mL min^{-1} NO, 50 mL min^{-1} O_2) were further introduced into the cell after the ventilation. When the adsorption-desorption of NO reached equilibrium state, the visible light was turned on and the subsequent dynamic FT-IR spectra were detected and recorded for 1 h.

3. Results and discussion

3.1. The rational design of C/BOC/B via theoretical calculation

DFT calculation, as a powerful tool, was applied to reasonably design the catalyst structure previous to experimental construction. The constructed models used in this article are shown in Fig. S4. Figure 1(a) shows the charge difference distribution of the BOC, C/BOC, and C/BOC/B catalysts. For pure BOC, the homogeneous and regular array of surface atoms determines the equivalent accumulation of electrons on each external atom, thus resulting in the random electron transfer and high recombination rate of photo-generated electrons and holes. Compared to the pure BOC, the external charge balance of C/BOC was disrupted after integrating C heteroatoms into the BOC lattice. Figure S5 presents the top view of the charge difference distribution of BOC and C/BOC. Obviously, the newly generated directional electron transfer channels are formed in C/BOC, which could be attributed to the different electronegativity between C and neighboring O atoms. A lower carried charges (Δq , Fig. 1(a)), calculated with Bader methods, of C atoms in C/BOC (-0.067 e) than O atoms in BOC (-0.623 e) can

Fig. 1. Charge difference distribution of BOC, C/BOC, and C/BOC/B: charge accumulation is in blue and depletion in yellow. The isosurfaces are set to $0.006 \text{ eV } \text{\AA}^{-3}$. Δq depicts the carried electrons of the selected atom and negative means electrons obtainment (a). Electronic location function (ELF) of BOC, C/BOC, and C/BOC/B (b). The density of state (DOS) of C/BOC/B, C/BOC, and BOC and projected density of states (PDOS) of Bi, C atom in C/BOC/B (c). Red, green, purple and brown spheres refer to O, Cl, Bi, and C respectively.

be observed. A stronger covalent bond between C-Bi in C/BOC (electronic location function results, Fig. 1(b)) also illustrates that the charge separation is enhanced, in comparison with that of O-Bi in BOC.

However, under the construction of elevated charge separation and directional delivery in the help of C-based electron transfer channels, the practical photocatalytic efficiency of C/BOC is still insufficiently ascribed to the limitation electrons that materials could supply. Thus an electron donor is particularly necessary, and this role is fulfilled admirably by Bi metal. From the charge difference distribution result (Fig. 1(a)), the electrons around Bi atom are localized and then transferred to the adjacent C atom, which generates a local region with high electron density, as confirmed by the Δq values of Bi (0.98 e) and C (−0.61 e) in C/BOC. Meanwhile, the ELF results in Fig. 1(b) also reveals that there is a much stronger covalent interaction between C atom and the neighboring atoms than that of C/BOC, indicating that a superior electron transfer channel has been created. And this oriented internal electric field, generated by the orientation of electrons delivery, significantly restrains the recombination of electron-hole pairs. Apparently, these localized excess electrons can be injected directionally to the catalyst surface via a C-based electron transfer channel, and directly participated in the photocatalysis.

An effective electron transfer is also supposed to enhance the absorption and activation of small molecules, including pollutants and other reactants. Table 1 shows the corresponding adsorption mechanisms of little molecules on different catalysts, which are simulated by DFT calculations. In comparison with BOC and CBOC, the changes of bond length and bond angle toward all molecules absorbed on C/BOC/B are more noticeable, which could make these small molecules easier to be activated during the adsorption stage.

Efficient light absorption is a prerequisite for the photocatalysis to proceed, and the light absorption capacity is primarily determined by the bandgap of photocatalysts. The DOS of the constructed BOC, C/BOC, and C/BOC/B models is further calculated to simulate the trend of bandgap change after electronic structure modification (Fig. 1(c)). Compared with the wide bandgap of BOC, a mid-gap state, above the valence band of C/BOC, is created by doped C atom, which could slightly enhance the absorption of visible light. Furthermore, the bandgap of C/BOC/B is drastically narrowed, revealing that this photocatalyst could absorb more visible light and generate more photo-excited carriers. This highly enhanced visible light response could be ascribed to the synergistic effects of doped C

heteroatom and deposited Bi metal. It can be obviously found that the bottom of the conduction band (CB) and the top of the valence band (VB) of C/BOC/B are obviously extended attributed to the doped C heteroatom and deposited Bi atom. On one hand, the electrons from the VB could be transferred to the doped C atom and then to the CB of Bi atom under the visible light irradiation. On the other hand, the photo-generated hot electron of Bi atoms could also be yielded under visible light irradiation owing to the SPR effect. And these hot electrons can be further transferred into the CB of BOC to participate in photocatalysis. Hence, it is expected that C/BOC/B should manifest more efficient photocatalytic performance than that of BOC or C/BOC after theoretical investigation.

3.2. The preparation and characterization of C/BOC/B photocatalysts

Encouraged by the theoretical calculation results, the precisely designed C/BOC/B photocatalyst with different amounts of Bi loading was further synthesized, and the morphology, microstructure, and component of the as-prepared samples were further characterized by various microscopic and spectroscopic methods. The TEM images of the prepared C/BOC/B nanocomposites are shown in Fig. 2(a). The samples show a flat 2D structure of C/BOC layer with uniformly distributed Bi QDs (mean size of 5.57 ± 0.84 nm) on its surface. The distinct lattice fringe of 0.22 and 0.27 nm can be clearly observed in high resolution TEM images (HRTEM, Fig. 2(b)), which are consistent with the (110) plane of the superficial Bi QDs and the basal C/BOC layer, respectively [29]. The morphology of pure BOC and C/BOC are also characterized by SEM (Fig. S6). The SEM images indicate that both BOC and C/BOC are presented with 2D morphologies.

To gain a better understanding of the structure and phase purity in the prepared C/BOC/B samples, XRD and XPS tests were further carried out. As shown in Fig. 2(c), all the diffraction peaks of the BOC match well with the standard XRD pattern of BiOCl (JCPDS no. 43-1456), and no other impurity phase was found. After doping with C element, an obvious shift toward the lower angle side can be observed from the (101) lattice plane of C/BOC and C/BOC/B, indicating a lattice expansion due to the incorporation of C atoms into the BiOCl lattice (Fig. S7).

Fig. 2(e) shows the high-resolution C 1s spectrum of these obtained samples. Apart from the three characteristic peaks at 284.6, 285.8, and 288.3 eV arising from the adventitious carbon [35], a newborn peak signal of C–Bi bond appeared at 282.5 eV both in C/BOC and C/BOC/B, indicating the successful incorporation of C dopants into BiOCl lattices to form C–Bi bonds [36]. By comparing the XRD spectra of C/BOC/B with other control groups, three obvious signals at 27.2° , 37.9° , and 39.6° began to emerge, which belong to (012), (104), and (110) diffraction planes of elementary Bi (JCPDS no. 05-0519), respectively (Fig. 2(c)). XPS survey scans further confirm that, there are only C, Bi, O, and Cl elements in C/BOC/B sample, no other elements could be found (Fig. 2(d)). Figure 2(f) shows the high-resolution Bi 4f spectrum of these samples. The two main

Table 1

The change of bond angle, bond length and adsorption energy for the small molecules on BOC, C/BOC, and C/BOC/B.

	Parameters	BOC	C/BOC	C/BOC/B
H ₂ O	$\angle \text{H-O-H}/^\circ$	104.34	103.48	105.15
	Ave. H-O/ $\text{\AA}$	0.974	0.975	0.979
	E_{ads}/eV	−0.200	−0.208	−0.317
O ₂	O-O/ $\text{\AA}$	1.287	1.275	1.324
	E_{ads}/eV	−0.797	−0.547	−1.546
NO	N-O/ $\text{\AA}$	1.183	1.181	1.201
	E_{ads}/eV	−0.253	−0.208	−0.956

Fig. 2. TEM (a) and HRTEM (b) images of C/BOC/B, inset of (a) is the size distribution of Bi QDs; (c) XRD patterns of different samples; The XPS spectra (d), high resolution C 1s (e), and Bi 4f (f) spectra of C/BOC/B.

binding energies at 159.2 and 164.4 eV are indicative of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ characteristic peaks toward Bi³⁺ in BiOCl [37]. And the Bi⁰ characteristic peaks appear at peaks of 158.4 (Bi $4f_{7/2}$) and 163.5 eV (Bi $4f_{5/2}$) [38], indicating the existent of elementary Bi on the surface of C/BOC layer, which consistent with the HRTEM and XRD results. It is worth noting that, both two dominating peaks, Bi $4f_{7/2}$ and Bi $4f_{5/2}$, show a negative chemical shift after C doping and Bi deposition, implying the surface electrons are tend to flow from Bi QDs to C/BOC layer.

3.3. Visible light photocatalytic NO removal and reactive species detection

Subsequently, the photocatalytic performance of the prepared C/BOC/B was evaluated for NO removal in the presence of visible light ($\lambda > 420$ nm). As shown in Fig. 3(a), a maximum NO removal ratio of 40.6% for C/BOC can be obtained in approximately 5 min, which is much higher than the 5.4% of pure BOC due to the large bandgap. However, an obvious decrease in removal efficiency is also observed on C/BOC after continuous irradiation. This result confirms that the C doping is an effective approach for improving the photocatalytic activity of BOC through electronic structure modulation, which is consistent with our previous theoretical calculations. And the decreasing trend might be attributed to the accumulation of intermediates

Fig. 3. (a) Evaluation of the photocatalytic efficiency of NO degradation under visible light irradiation; (b) The cycling test of C/BOC/B under visible light irradiation.

on the surface of C/BOC. As a stark contrast, the removal efficiency of the as-prepared C/BOC/B sample approached to the maximum value of 53.0% within 8 min, and no obvious decay can be seen after continuous irradiation, indicating that the modification of Bi QD can further improve the photocatalytic performance of C/BOC. As shown in Fig. 3(b), after five cycles of photocatalytic experiments, the removal efficiency toward the C/BOC/B sample is only slightly decreased by 8.9%, indicating its relatively high stability and reusability.

3.4. Charge separation, transportation, and transformation mechanisms

In order to understand essential reasons for the enhancement in photocatalytic activity, the characterization of optical properties and energy band structures of the as-prepared photocatalysts were carried out. Figure 4(a) shows the UV-vis DRS of different samples. In contrast to the pristine BOC, which can only respond to ultraviolet light, the visible light adsorption intensity of C/BOC, especially the C/BOC/B, has been improved obviously. The C/BOC/B exhibits a full adsorption phenomenon in the visible region due to the SPR effect of the Bi QDs. Besides, as shown in Fig. 4(b), the bandgaps of BOC and C/BOC, are 3.24 and 3.10 eV, respectively, which are estimated from the intercepts of the tangents to the plots of $(\alpha h\nu)^2$ vs. photoenergy. The trend is consistent with theoretical calculation (Fig. 1(c)). The decreased bandgap will lower the energy requirement for the excitation of the photo-generated charge. Therefore, the enhanced visible light absorption and the decreased bandgap reveal that the loading of Bi QDs and/or the doping with C are efficient methods to improve the utilization of visible light and accelerate the production of photo-generated charge.

To explore the mechanism of electron delivery, charge mobility has also been analyzed. As shown in Fig. 4(c), the PL intensity of C/BOC is decreased relative to the pure BOC, and after loading Bi QDs, the PL intensity of C/BOC/B is further decreased, which reveals that the loaded Bi QDs could further strengthen the internal electric field generated by C atom to promote the electrons directional delivery. To understand how the separated charge carriers work in photocatalysis, the DMPO spin-trapping ESR technique was employed to detect active species under visible light irradiation. As shown in Fig. 4(d), the electron sacrificial agent is rapidly depleted in C/BOC/B under light irradiation, but that of C/BOC is still re-

Fig. 4. (a) UV-vis DRS of different samples; (b) The plot of $(\alpha h\nu)^2$ vs photon energy based on UV-vis DRS spectra; (c) PL spectra of different samples; DMPO ESR spin-trapping for electrons (d), superoxide radical (e), and hydroxyl radical (f).

sidual. This result illustrates that more free electrons exist in the C/BOC/B than C/BOC sample as the photo-generated electrons could transfer in the path of Bi QDs $\rightarrow$ C/BOC $\rightarrow$ adsorbed O_2 molecule and prevent the recombination of charge carriers in C/BOC/B. As for the pure BOC, the consumption of electron sacrificial agents is more negligible ascribing to the delocalization of photo-generated electrons. Figure 4(e) indicated the $\cdot O_2^-$ radical signals in different samples. The increased $\cdot O_2^-$ radicals are extremely dependent on the localized electrons and directional electron transport, which enable the adsorbed O_2 molecules to acquire more electrons for activation ($O_2 + e^- \rightarrow \cdot O_2^-$). After doped with C, a stronger $\cdot O_2^-$ signal can be detected for C/BOC sample in comparison with pure BOC, which confirms that the capacity of directional electron transport can be enhanced by C doping, and enable the localized electrons to be injected into O_2 more efficiently.

To further improve the capacity of O_2 activation, metallic Bi QDs are loaded onto the surface of C/BOC. Encouragingly, the C/BOC/B sample indeed exhibited the maximum value of the $\cdot O_2^-$ signal, which confirms that the introduction of Bi QDs can promote the activation of O_2 by strengthening the electron supply on the basis of C/BOC. The above-mentioned ESR results fully demonstrated that the C doping together with Bi QDs loading is a promising strategy to improve the activity of BOC via the enhancement of the electron supply and directional electron transport. In addition, a similar trend toward $\cdot OH$ rad-

icals detection is also observed in Fig. 4(f), the increased $\cdot OH$ radicals could be generated from the oxidation of OH^- by the left photo-generated holes ($OH^- + h^+ \rightarrow \cdot OH$) and the step reduction of $\cdot O_2^-$ ($\cdot O_2^- \rightarrow H_2O_2 \rightarrow \cdot OH$). On BOC, the negligible $\cdot OH$ signal illustrates that the left holes and $\cdot O_2^-$ in BOC are insufficient, and unable to support the generation of $\cdot OH$ owing to the severe restriction of photo-induced electrons originated from the strong electronegativity of O atoms in BOC. However, this situation has been improved very well in C/BOC and C/BOC/B. After the modulation of Bi QDs loading and/or C doping, the electrons excitation and charge transport can be effectively promoted, which is well consistent with the theoretical DFT results in Part 3.1.

3.5. In situ FT-IR investigation on the photocatalytic NO removal mechanism

To investigate the pathway and mechanism of the photocatalytic NO purification process, the corresponding IR absorption spectra of the major reaction intermediates and final products on the surface of different photocatalysts are accurately evaluated by in situ FT-IR measurements. As shown in Fig. 5(a), under visible light irradiation, significant spectral changes have been observed in the dynamical FT-IR spectra of different samples. Compared with the pure BOC, the gradually increased adsorption intensity of the target NO_3^- product are detected at 1279, 1482, and 1525 cm^{-1} [39,40], while the gradual consumption of NO_2^- product (822, 860, 898, and 1206 cm^{-1}) [30,41,42] in FT-IR spectra of C/BOC and C/BOC/B can be observed, indicating the synergistic effects of C doping and Bi loading could further enhance the ability of NO conversion and improve photocatalytic selectivity for NO_3^- .

In order to elaborate the underlying mechanism for the enhancement of selective activation toward reactants or intermediates in photocatalysis, the adsorption energies of these major intermediates and products in different samples are further calculated through the DFT method. The NO, NO_3^- , NO_2^- , and other major intermediates including N_2O_2 (1137 and 1630 cm^{-1}) [39,43] and NO_2 (1327–1465 and 1598 cm^{-1}) [42,44,45] which could be obviously observed in FT-IR spectra are all taken into account. The photocatalytic NO oxidation mechanism is deduced from the FT-IR spectra as shown in Fig. 5(b). It is clearly showed that all the energy demands for each step in C/BOC/B are much lower than that on C/BOC or pure BOC, indicating that the adsorption energy of adsorbed $NO \rightarrow N_2O_2 \rightarrow NO_2/NO_2^- \rightarrow NO_3^-$ process is an increasing tendency, and the reactions of these exothermic processes are energy favorable in C/BOC/B.

Moreover, the IR spectra of C/BOC/B are smooth that except the peaks of N_2O_2 , almost no other intermediates peaks could be detected on the surface. The accumulation of N_2O_2 is ascribed to the rapid consumption of NO with the relatively slow consumption of N_2O_2 . Therefore, the transformation of N_2O_2 to NO_2/NO_2^- is the rate-limiting step. Unlike C/BOC/B, the accumulation of N_2O_2 on the surface of BOC (Fig. 5(a)) resulted from the thermodynamic deficiency in transformation of N_2O_2 to NO_2/NO_2^- (as shown in Fig. 5(b), 3th step), which limits the

Fig. 5. (a) In situ FT-IR spectra of the photocatalytic NO oxidation process over different samples; (b) The DFT calculated adsorption energies of the intermediates and products involved in the reaction process of different samples.

conversion of NO and further lead to the accumulation of NO (1017, 1066, and 1106 cm^{-1}) [39,46,47] in turn. Besides, the adsorption and activation of NO are vital before it can be oxidized. Compared with C/BOC, the enhanced surface electron density of C/BOC/B endows outstanding adsorption and activation of NO attributed to the incorporation of Bi QDs. Overall, the in situ FT-IR results and adsorption energy profile suggest that the enhanced adsorption of reactants and intermediates could promote the overall reaction efficiency and selectivity in photocatalytic NO conversion.

4. Conclusions

In summary, we have successfully fabricated a unique Bi QDs implanted C-doped BiOCl photocatalyst through the simultaneous integration of C heteroatom and plasmonic Bi QD into BOC. The as-prepared C/BOC/B exhibited excellent photocatalytic activity and stability for NO removal. As confirmed by the theoretical DFT calculation and experimental characterization results, the synergistic effects of C doping and plasmonic Bi loading should be essential for performance enhancement. On the surface of C/BOC/B, the regular arraying of external atoms has been disturbed after C doping, and a directional electron transfer channel was constructed. The SPR effect of deposited plasmonic Bi QD enables an obvious enhancement of visible light utilization and boost the generation of hot electron. The hot electrons from Bi QD along with the photo-excited electrons from the interior of BOC can directly transfer to the surface of BOC with a suppressive recombination rate of carriers via the preformed electron delivery channel. Therefore, the increased external charge density can promote the adsorption and activation of reactant molecular, and enhance the overall NO purification efficiency. This novel and efficient synergic strategy has simultaneously achieved the enhanced electron donating, efficient solar utilization, promoted directional electron delivery as well as the suppressed carrier recombination toward BOC catalyst. This work could provide a new perspective and strategy for the design of efficient photocatalyst extended to other 2D nanomaterials for various applications.

Acknowledgments

The authors also acknowledge AM-HPC in Suzhou, China for computational support.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1430–1438 doi: 10.1016/S1872-2067(20)63612-9

**Bi quantum dots implanted 2D C-doped BiOCl nanosheets:
Enhanced visible light photocatalysis efficiency and reaction
pathway**

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A novel Bi quantum dots implanted C-doped BiOCl photocatalyst was designed and fabricated to enhance the efficiency of purifying NO in air under visible light irradiation and inhibit the generation of toxic intermediates simultaneously.

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Bi量子点修饰的C掺杂二维BiOCl纳米片：增强的可见光光催化活性和反应路径

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摘要: 异相光催化技术已经受到了国内外广泛关注, 逐渐成为利用太阳能解决能源与环境问题的有效手段。典型异相光催化反应的步骤包括光子捕获、载流子分离与迁移、以及载流子参与光化学氧化还原反应, 因此, 开发太阳能利用率高、电

荷复合率低、载流子迁移效率高的高活性、高稳定性的光催化剂在环境修复和太阳能转化的实际应用中具有极其重要的意义。在半导体光催化剂上同时集成杂原子掺杂和表面等离子共振效应可以有效提高可见光利用率和电荷分离,实现更好的太阳光利用和光催化效率。因此,我们设计了一种新型的Bi量子点修饰的C掺杂BiOCl光催化剂(C/BOC/B)来去除空气中NO_x污染物。

首先,通过密度泛函理论(DFT)评估了Bi负载和C掺杂协同提高BiOCl光催化性能的可行性。理论结果证实,掺杂的C原子可以创造电子通道,诱导电荷定向地从Bi量子点转移到BiOCl (BOC);同时,具有等离子体效应的Bi量子点可以充当光捕获中心和电子供体。因此,C原子掺杂和Bi量子点负载的协同作用,有望进一步提高材料的光催化性能。随后,通过简单的溶剂热法合成了C/BOC/B样品。SEM和TEM图像显示了BOC, C/BOC和C/BOC/B样品的形貌,同时也显示了原位生成的Bi量子点均匀地分布在BOC的表面。XRD、XPS结果表明,C原子已成功掺入BOC的晶格,并且C/BOC表面存在Bi元素。同时,根据Bi的主峰在材料进行Bi负载后向负方向移动,可以推测出电子倾向于从Bi量子点流向材料本身。接着,在可见光条件下评估了C/BOC/B去除NO的光催化性能,与原始BOC或C/BOC相比,该C/BOC/B光催化剂对NO的净化表现出优异的光催化效率,去除率达到53.0%。紫外-可见光谱显示,C/BOC/B的光吸收扩展到了可见光范围。利用ESR光谱发现,C/BOC/B上的ESR信号较强,说明C/BOC/B具有较好的氧化能力,同时也证明了光生载流子在C/BOC/B上可以通过电子传递通道实现有效分离。最后,通过原位傅里叶变换红外光谱(FT-IR)结合DFT计算对NO转化的反应途径和机理进行了研究结果表明,在C/BOC/B样品上反应物与中间产物增强的吸附能有效提高材料的光催化效率,同时抑制中间产物的形成,提高目标产物选择性,可见,设计并制备的C/BOC/B表现出优异的光催化活性和脱除NO的稳定性。理论DFT计算和实验表征结果证实,C掺杂和等离子体Bi负载的协同效应对于性能的增强至关重要。本文为有效光催化剂设计提供了新的视角和策略,可进一步激发2D纳米材料的光催化性,从而推动它在异质光催化中的广泛应用。

关键词: BiOCl; C掺杂; Bi量子点; 光催化; 反应机理

收稿日期: 2020-02-13. 接受日期: 2020-03-10. 出版日期: 2020-09-05.

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基金来源: 国家自然科学基金(21822601, 21777011); 中央高校基本科研业务费专项基金(ZYGX2019Z021, 2672018ZYGX2018J088); 高等学校学科创新引智计划; 国家万人计划和四川省科学技术厅重点研发计划(2019YFG0319).

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